

Energy band in semiconductors.

Energy bands in solids.

→ Isolated atoms have discrete energy levels but in solid, energy bands are present due to interaction between atoms when they unite to form a solid. There are two distinct energy bands in which electrons may exist. They are valence band and conduction band and are separated by an energy gap in which no electron can normally exist and is called forbidden band/gap.

i) valence band.

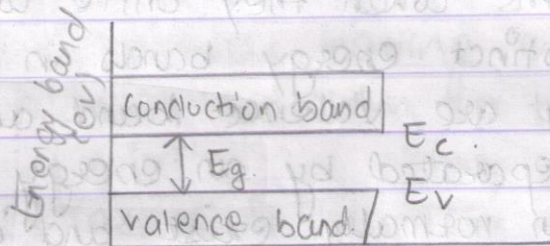
→ The highest filled energy band which includes electrons shared in covalent bond or electrons transferred in ionic bond is known as valence band. If sufficient amount of energy is given to an electron in this band, the electron is freed from the atomic structure. Such an electron is said to possess enough energy to be in the conduction band.

The energy level corresponding to the top of the valence band is denoted by E_v .

ii) Conduction band

→ The band of permitted energy level just above the valence band in which free electrons called conduction electrons are present is called conduction band. The conduction electrons are free to move in presence of external electric field. Due to interaction between

atoms there is range of energy from minimum zero to maximum possible energy called Fermi energy, E_f . This band is partially filled or empty. The energy level corresponding to bottom of the conduction band is denoted by E_c , E_v .



Fermi energy is the maximum possible energy possessed by conduction electrons in conduction band at absolute temp ($T=0\text{ K}$) is known as fermi energy.

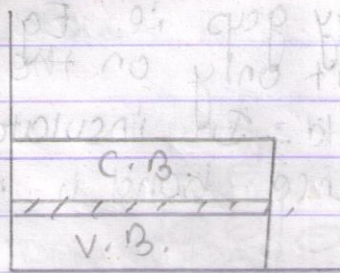
Forbidden band.

→ The conduction band has higher energy level than the valence band. There is a forbidden energy region space between conduction and valence band, known as forbidden band.

→ The energy gap between conduction and valence band is denoted by E_g .

Substances are divided into conductors, semi conductors and insulators on the basis of energy gap. In conductors, valence band and conduction band overlap each other.

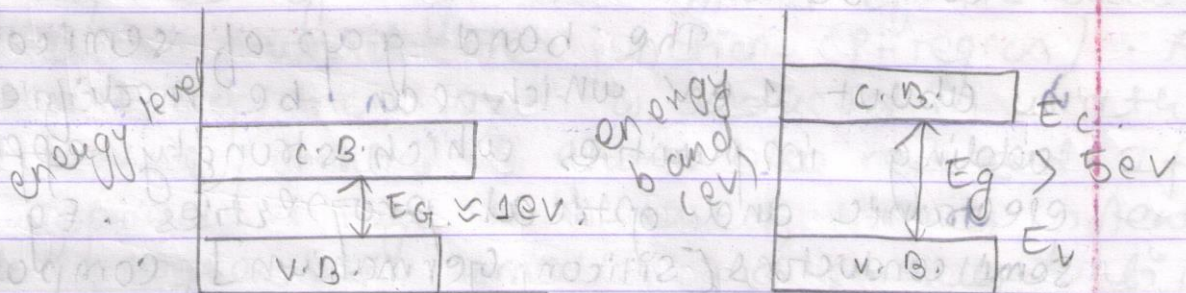
energy
band



Conductors.

Thus, metals are good conductors. Electrons in bands are distributed in accordance to Pauli's exclusion principle. (No two electrons are present in same quantum state)

Band structure of semiconductors and insulators are similar, except that the forbidden band (gap) in semiconductor is comparatively narrow.



Semiconductors have low energy gap of order of 1eV . At absolute temperature, semiconductor is a perfect insulator.

Thermal energy can promote few electrons from valence band to conduction band.

Insulators have high energy gap i.e. $E_g > 5 \text{ eV}$. They can conduct electricity through it only on the application of very strong electric field. In insulator, conduction band is empty and valence band is fully occupied by electrons.

★ Semi-conductors.

Semi-conductors are material which have electrical conductivities ~~of~~ lying betⁿ those of good conductors and insulators. At room temperature, such materials have conductivities considerably lower than those of conductors and much higher than those of insulators. An even more important property of semi conductor is that their resistance depends largely on various factors and therefore, it can be controlled.

The band gaps of semiconductor is about 1 eV which can be modified by adding impurities which strongly effect their electronic and optical properties. Eg elemental semi conductors [Silicon, Germanium], compound semiconductors [Aluminium phosphide (AlP), Gallium arsenide (GaAs), Indium phosphide (InP)].

Material	Resistivities ($\Omega \text{ m}$)
1) Conductor	10^{-8}
2) Semi conductor.	$10^{-4} - 0.5$
3) Insulator	10^{12}

Types of semiconductors

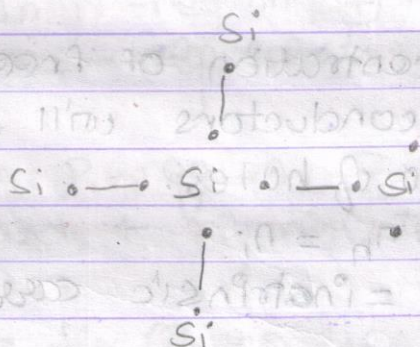
1) Intrinsic semiconductors (Pure)

2) Extrinsic semiconductors (Impure)

1) Intrinsic semiconductors

→ An intrinsic semiconductor is one which is made up of the semiconductor ^{material} in its extremely pure form. i.e. undoped semiconductor like Si, Ge.

→ In such semiconductors, all the valence electrons take part in covalent bond ~~formation~~ formation



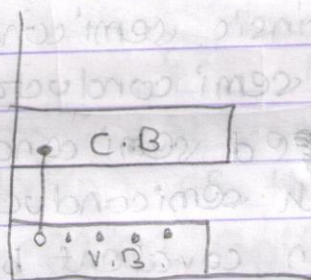
and no electron is free to cause conduction at 0 K.

→ Thus, the semiconductors at 0 K act as insulators. As the temperature of semiconductor is increased, valence electrons get sufficient thermal energy and break the covalent bond.

→ After being free from covalent bonding, electrons escape to the conduction band and leave behind an empty space called a hole which moves

in opposite direction to the electrons

→ A hole is represented by a small circle.
When a free electron is generated, simultaneously a hole is too created. Thus, free electrons and holes are generated in a pair form.



Thus, the concentration of free electrons and holes in intrinsic semiconductors will be always equal.
i.e. no. of electrons = no. of holes.

$$n_e = n_h = n_i$$

n_i = intrinsic carrier concentration

A hole is not a particle but for all practical purposes, it is taken as a positively charged particle capable of conducting current.

Electrons and holes have different properties like mobility, effective mass, etc.

Q) Extrinsic semiconductors. (Impure).

→ Intrinsic semiconductor has a little current conduction capability at room temperature. However, it

can be increased many times by adding very small amount of impurity (one atom per million atoms of semiconductor) to the semiconductor in the process of crystallization. This process is called doping and the doped material is called extrinsic or impure semiconductor. Ge and Si are tetravalent. So, doping material (dopant) may be either trivalent or pentavalent. Depending upon the nature of impurity added, there are two types of extrinsic semiconductors. They are.

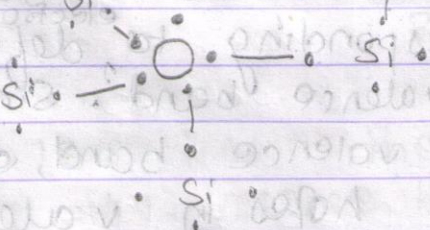
1) N type

2) P type.

1) N type. (Donor extrinsic or semiconductor)

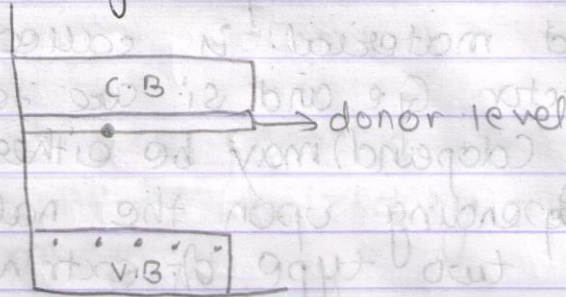
→ When small amount of pentavalent impurity (like As, Bi, Sb) is added to the semiconductor during its growth, the resulting crystal is called N type semiconductor.

→ When pentavalent atom is introduced in semiconductor, four out of each five valence electrons form covalent bond with four electrons of semiconductor and fifth valence electron remains free to move.



→ The energy level of fifth electron lies slightly below conduction band and called donor level. Each

pentavalent impurity atom donates one free electron to the semiconductor. Such impurities are called N type or donor impurities. In this type of semiconductor; electrons are majority charge carriers and holes are minority charge carriers.



2) P-type

When a small amount of trivalent impurity like B, Ga is added to a pure semiconductor material during its formation, the resulting crystal is called P-type extrinsic semiconductor.

On doping trivalent impurity into semiconductor, it forms three covalent bonds with semiconductor and fourth bond is not completed due to lack of one electron. Thus, trivalent atom has tendency to accept one electron from a neighbouring semiconductor atom to complete fourth bond.

The transferred electron leaves behind a hole. The energy level corresponding to ^{electron} deficiency is located just above the valence band. Since, acceptor level lies close to the valence band, small amount of energy even create holes in valence band. Hence holes are majority charge carriers in P-type extrinsic semiconductor.

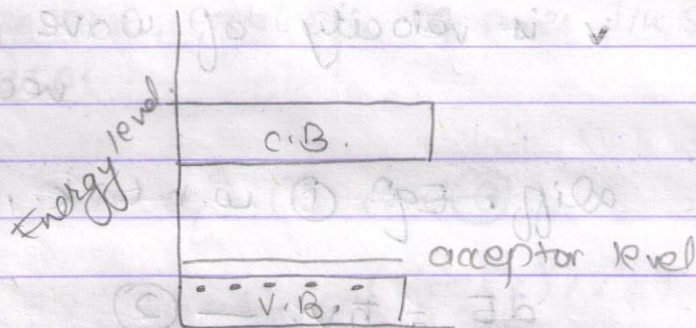
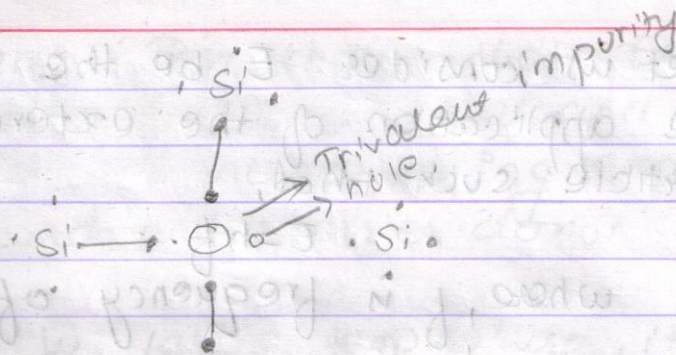
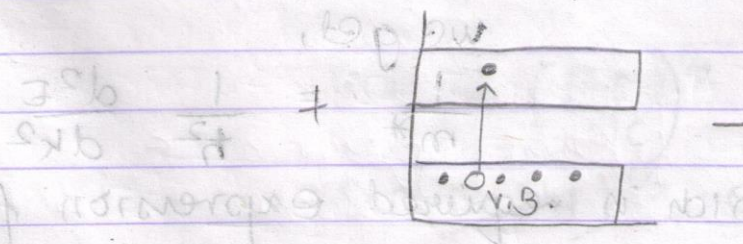


Fig. 2 Energy level diagram for P-type

Effective mass (m^*)

→ An electron in crystal may behave as if it has a mass different from the free electron mass (m_0). There are crystals in which effective mass of the carriers is much larger or much smaller than m_0 . The mass of one electron/hole during the application of external electric field is called effective mass.



let us consider E be the energy provided by the application of the external electric field to the particle such that,

$$E = hf.$$

where, f is frequency of particle

$$\text{or, } E = \hbar \omega$$

$$\text{or, } E = \hbar v k. \quad \text{--- (1)}$$

v is velocity of wave, k is wave vector, $k = \frac{2\pi}{\lambda}$

diff. Eqⁿ (1) w.r.t. k , we get

$$\frac{dE}{dk} = \hbar v. \quad \text{--- (2)}$$

Again, diff eqⁿ (2) w.r.t. t .

$$\frac{1}{\hbar} \frac{dE}{dt} = \frac{dv}{dt}$$

$$\text{or, } \frac{1}{\hbar} \frac{d^2 E}{dk^2} \cdot \frac{dk}{dt} = \frac{dv}{dt}$$

$$\text{or, } \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \frac{d(\hbar k)}{dt} = \frac{dv}{dt} \quad \text{--- (3)}$$

Comparing eqⁿ (3) with Newton's second law.

$$F = m^* a.$$

we get,

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

which is required expression for effective

motion of charge particle in electric field.

★ Electrical conductivity in semiconductor
the amount. → The current density is defined as
the amount of current passing unit area perpendicular
flow of current

$$\text{i.e. } J = \frac{I}{A} \quad \text{--- (1)}$$

Again, we have $I = neV_d A$ --- (2)

n = no. of electrons / volume

V_d = drift velocity

A = cross section area.

$$J = neV_d$$

current density due to electron is $J_n = neV_{dn}$.
 V_{dn} = ~~current~~ drift velocity of
electrons.

Similarly, due to holes.

$$J_p = peV_{dh}$$

V_{dh} = drift velocity of holes.

So, total current density in semiconductor is given
by,

$$\begin{aligned} J &= J_n + J_p \\ &= neV_{dn} + peV_{dh} \\ &= e(nV_{dn} + pV_{dh}) \quad \text{--- (3)} \end{aligned}$$

Again, $V_d \propto E$

$$\text{or, } V_d = \mu E \quad \text{--- (4)}$$

where μ is proportionality constant called

mobility of charge carrier. which is defined as drift velocity acquired by a charge carrier per unit applied electric field.

$$\text{or, } \mu = \frac{v_d}{E}$$

From (3) and (4), we have,

$$J = e(n\mu_e E + p\mu_p E)$$

$$J = eE(n\mu_e + p\mu_p) \quad \text{--- (5)}$$

Again, we have,

$$J = \sigma \cdot E \quad \text{--- (6)}$$

Comparing eqⁿ (5) and (6)

$$\sigma = e(n\mu_e + p\mu_p) \quad \text{--- (7)}$$

where, σ is conductivity.

For intrinsic semiconductor,

$$n = p = n_i$$

So, eqⁿ (7) becomes

$$\sigma = n_i e (\mu_e + \mu_p)$$

conductivity of intrinsic semiconductor

Q2.

A rod of intrinsic semiconductor (Si) is 1 cm long and has a diameter of 1 mm. At room temp, the conductivity is $4.32 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$. Find the intrinsic concⁿ in the Si as mobilities of electrons and holes are $\mu_e = 0.13 \frac{\text{m}^2}{\text{Vs}}$ $\mu_p = 0.05 \frac{\text{m}^2}{\text{Vs}}$.

→ Here,

For intrinsic semiconductor,

$$\sigma = n_i e (u_e + u_p)$$

$$4.82 \times 10^{-4} = n_i (1.6 \times 10^{-19}) (0.13 + 0.05)$$

$$n_i = 1.5 \times 10^{16} / \text{m}^3$$

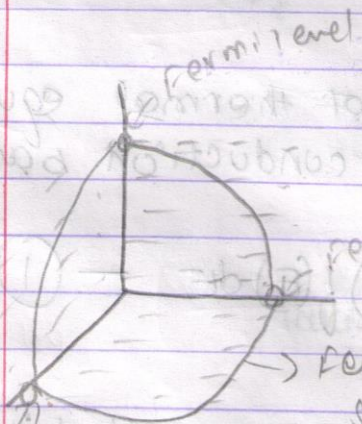
FERMI LEVEL

→ The energy level in which maximum number of electrons are found in ground state is defined as fermi level.

→ It is given by

$$E_F = \frac{\hbar^2 k_f^2}{2m}$$

where, k_f is wave vector on radius of Fermi sphere.



$$E_F = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2$$

N = no. of electrons.

L = length of 1-D potential well

m = mass of charge carrier

★ Density of states

→ It is defined as the no. of levels or the electronic states within the unit energy range about a particular value of energy.

$$D(E) = \frac{dn}{dE}$$

dn → no. of electronic states

dE → small difference in energy.

$$D(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

E = Energy range.
(particular)

LiQ sure (→ holes + electrons both)

★ Carrier concentration of electrons in conduction band of intrinsic semiconductor

→ Under the condition of thermal equilibrium, the concentration of electrons in conduction band is given by

$$n = \int_{E_c}^{\infty} D(E) f(E) dE \quad \text{--- (1)}$$

where, $f(E)$ → Fermi-Dirac probability funcⁿ.

$$D(E) = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2}$$

$$\text{and } f(E) = \frac{1}{1 + e^{(E - E_f)/k_B T}}$$

Substituting value of $f(E)$

At room temperature $(E - E_f) \gg k_B T$.

So, we can neglect 1 because something very large in power of e is a very large quantity. So,

$$f(E) = e^{[-(E - E_f)/k_B T]}$$

Substituting these values in eqn (1)

$$n = \int_{E_c}^{\infty} \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} e^{[-(E - E_f)/k_B T]} dE$$

or, $n \neq$

$$\begin{aligned} e^{-(E - E_f)} &= e^{-(E - E_f + E_c - E_c)} \\ &= e^{-[(E - E_c) - (E_f - E_c)]} \\ &= e^{-(E - E_c)} \cdot e^{(E_f - E_c)} \end{aligned}$$

or, $n =$

$$\text{or, } n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{[(E_f - E_c)/k_B T]} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{[-(E - E_c)/k_B T]} dE$$

Let $\frac{E - E_c}{k_B T} = x$

$$\therefore dE = k_B T dx$$

$$\text{If } E = E_C, x = 0.$$

$$E = \infty, x = \infty$$

$$\text{or, } n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_F - E_C)}{k_B T}} \int_0^\infty (k_B T)^{1/2} x^{1/2} e^{-x} dx.$$

$$\text{or, } n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_F - E_C)}{k_B T}} (k_B T)^{3/2} \int_0^\infty x^{1/2} e^{-x} dx$$

$$\text{Again, we have, } \int_0^\infty x^{1/2} e^{-x} dx = \frac{\sqrt{\pi}}{2}.$$

$$\text{or, } n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_F - E_C)}{k_B T}} (k_B T)^{3/2} \frac{\sqrt{\pi}}{2}$$

$$\text{or, } n = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{\frac{(E_F - E_C)}{k_B T}}.$$

$$\text{or } n = N_C e^{\frac{(E_F - E_C)}{k_B T}}$$

$$\text{where } N_C = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2}$$

Concentration of holes in valence band
under the condition of thermal equilibrium
the concentration of holes in valence band is given
by.

$$P = \int_{-\infty}^{E_v} D_h(E) f_h(E) dE. \quad \text{--- (1)}$$

where,

$$D_h(E) = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2}.$$

$$\text{and } f_h(E) = 1 - f_e(E)$$

$$\text{and } f_h(E) = 1 - \frac{1}{1 + e^{(E - E_f)/k_B T}}.$$

$$= \frac{e^{(E - E_f)/k_B T}}{1 + e^{(E - E_f)/k_B T}}.$$

At room temperature,

$$(E - E_f) \ll k_B T.$$

$$f_h(E) = e^{(E - E_f)/k_B T}$$

Substituting value of $D_h(E)$ and $f_h(E)$ in eqn (1)

$$P = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} \int_{-\infty}^{E_v} (E_v - E)^{1/2} e^{(E - E_f)/k_B T} dE.$$

$$P = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} \int_{-\infty}^{E_v} (E_v - E)^{1/2} e^{\frac{(E_v - E_f)}{k_B T}} e^{-\frac{(E_v - E)}{k_B T}} dE$$

$$P = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}} \int_{-\infty}^{E_v} (E_v - E)^{1/2} e^{-\frac{(E_v - E)}{k_B T}} dE$$

$$p = \int_0^\infty \frac{E_v - E}{k_B T} = x$$

$$dE = -dx k_B T$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_n^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}} \int_0^\infty \frac{x^{1/2} (k_B T)^{1/2} e^{-x} dx}{k_B T}$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_n^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}} \int_0^\infty x^{1/2} (k_B T)^{1/2} e^{-x} dx k_B T$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_n^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}} \cdot (k_B T)^{3/2} \int_0^\infty x^{1/2} e^{-x} dx$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_n^*}{\hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}} \cdot (k_B T)^{3/2} \frac{\sqrt{\pi}}{2}$$

$$p = 2 \left(\frac{m_n^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{\frac{(E_v - E_f)}{k_B T}}$$

$$\text{or, } p = N_v \cdot e^{(E_v - E_f)/k_B T}$$

which is reqd. expression for concentration of holes in valence band

Fermi level in intrinsic semiconductor,

In intrinsic semiconductor $n=p=n_i$

$$\text{or, } N_c e^{\frac{-(E_f - E_c)}{k_B T}} = N_v e^{\frac{(E_v - E_f)}{k_B T}}$$

$$\text{or, } \frac{N_c}{N_v} = e^{\frac{(E_v - E_f - E_f + E_c)}{k_B T}}$$

$$\text{or, } \frac{N_c}{N_v} = e^{\frac{(E_v + E_c - 2E_f)}{k_B T}}$$

Taking $\ln$ on both sides

$$\ln\left(\frac{N_c}{N_v}\right) = \frac{E_v + E_c - 2E_f}{k_B T}$$

$$\text{or, } E_f = -\frac{k_B T}{2} \ln\left(\frac{N_c}{N_v}\right) + \frac{E_v + E_c}{2}$$

$$\text{or, } E_f = \frac{k_B T}{2} \ln\left(\frac{N_v}{N_c}\right) + \frac{E_v + E_c}{2}$$

Also,

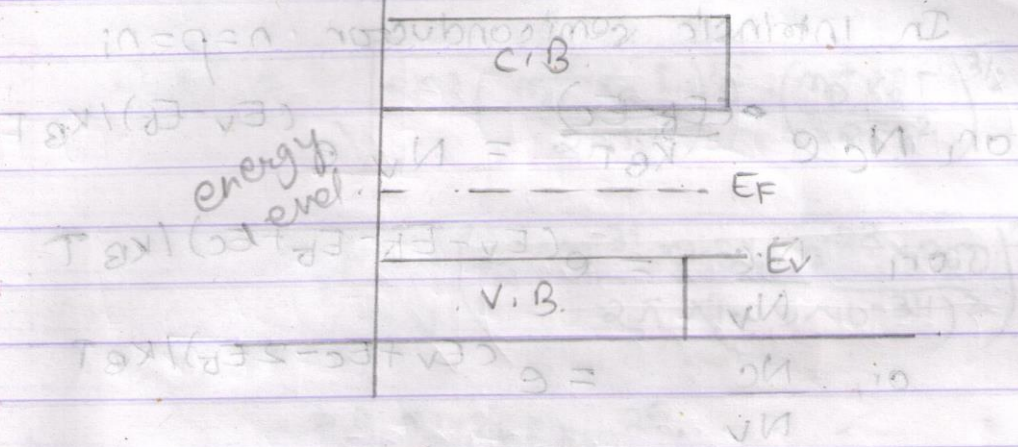
$$E_f = \frac{E_v + E_c}{2} + \frac{3k_B T}{4} \ln\left(\frac{m_n^*}{m_p^*}\right)$$

Condition

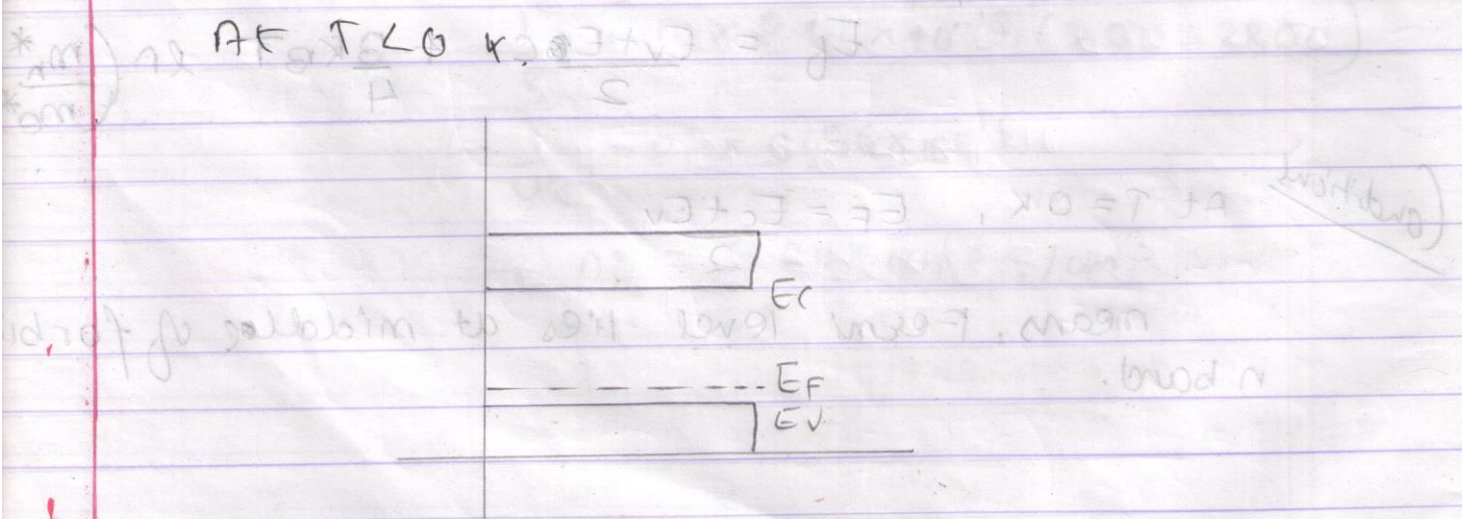
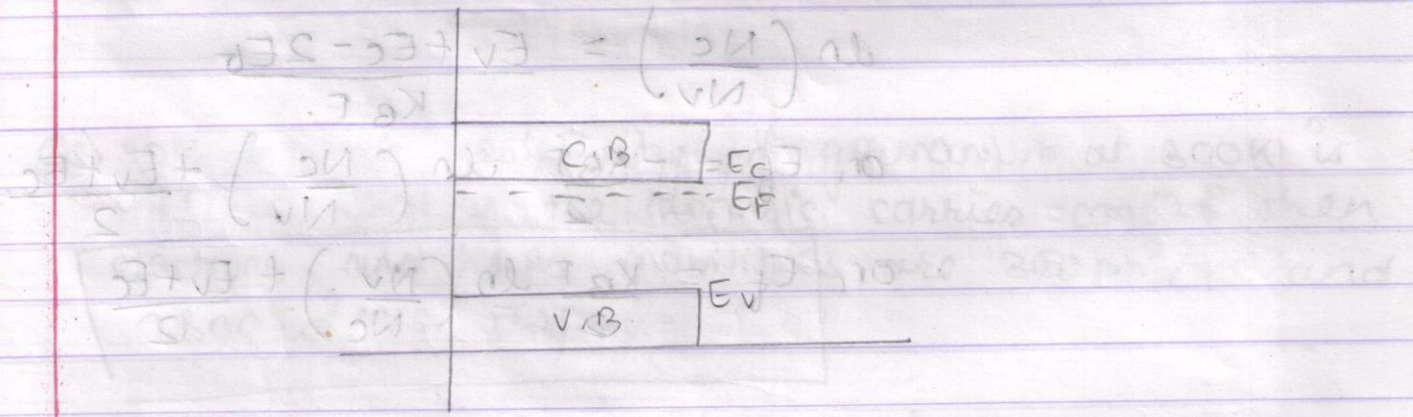
$$\text{At } T=0\text{ K, } E_f = \frac{E_c + E_v}{2}$$

means, Fermi level lies at middle of forbidden band.

Form level in intrinsic semiconductor



At $T > 0$ K, no net p-n



law of mass action.

It states that for a given semiconductor, the product of electron and hole concⁿ is constant at a given temperature and equal to the square of intrinsic carrier concentration.

$$n_i^2 = np = N_c e^{(E_F - E_C)/k_B T} \cdot N_v e^{(E_V - E_F)/k_B T}$$

$$= N_c \cdot N_v e^{(E_F - E_C + E_V - E_F)/k_B T}$$

$$= N_c \cdot N_v \cdot e^{(E_V - E_C)/k_B T}$$

$$= N_c \cdot N_v e^{-\frac{(E_C - E_V)}{k_B T}}$$

$$= N_c \cdot N_v e^{-E_g/k_B T}$$

$$n_i = \sqrt{N_c \cdot N_v} e^{-E_g/2k_B T}$$

where, $E_g = E_C - E_V$ is called band gap energy or energy gap.

Qs) Evaluate intrinsic carrier concⁿ of Ge. at room temp. given that effective mass of holes and electrons are equal to $m_e^* = m_h^* = m_0 = 9.1 \times 10^{-31} \text{ kg}$ and band gap energy is 0.68 eV.

→ Here,

$$N_c = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2}$$

$$n_B = 1.38 \times 10^{23}$$

$$N_V = 2 \left(\frac{m_p^* K_B T}{2\pi \hbar^2} \right)^{3/2}$$

$$n_i = \sqrt{2 \times 2 \left(\frac{m_e^* K_B T}{2\pi \hbar^2} \right)^{3/2} \cdot \left(\frac{m_p^* K_B T}{2\pi \hbar^2} \right)^{3/2} \cdot e^{-\frac{E_g}{2K_B T}}}$$

$$= 2 \sqrt{\left(\frac{9.1 \times 10^{-31} \times 1.38 \times 10^{-23} \times 300}{2\pi \times (1.05 \times 10^{-34})^2} \right)^3 \cdot e^{-\frac{0.68 \times 10^{-19}}{2 \times 1.38 \times 10^{-23} \times 300}}}$$

$$= 2 \times 1.268 \times 10^{25}$$

$$= 1.29 \times 10^{25}$$

Q5) The intrinsic resistivity of germanium at 300K is 47 Ωcm . what is the intrinsic carrier concⁿ when electrons and holes mobilities are 300 cm^2/Vs and 3800 cm^2/Vs resp.

$$\sigma = n_i e (\mu_e + \mu_p)$$

$$\frac{1}{\sigma} = n_i \times 1.6 \times 10^{-19} (300 + 3800)$$

$$\frac{1}{47} = n_i \times 6.56 \times 10^{-16}$$

$$n_i = 3.24 \times 10^{13} / \text{cm}^3$$

Q5) Given that no. of electrons/length of a crystal is 0.5 electrons/Å. Calculate the Fermi energy.

→ We have,

$$L = 0.5 \text{ electrons/Å}$$

$$= 0.5 / 10^{-10} \text{ m}$$

$$= 0.5 \times 10^{10} / \text{m}$$

$$(2.37 \text{ eV})$$

Q6) The energy $E_F = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2$

$$= \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \times \left(\frac{0.5 \times 10^{10} \times \pi}{2} \right)^2$$

$$= 3.736 \times 10^{-19} \text{ J}$$

$$= \frac{3.736 \times 10^{-19} \text{ eV} \times 1.6 \times 10^{-19}}{1.6 \times 10^{-19}} = 2.335 \text{ eV}$$

Q7) The energy near the valence band of a crystal is given by $E = Ak^2$ where, $A = 10^{-31} \text{ Jm}^2$ and an electron wave vector $k = 10^{10} \text{ m}^{-1}$ is removed from an orbital in the completely filled valence band. Determine its effective mass, velocity, momentum and energy of hole.

→ Solⁿ:

We have,

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

$$E = Ak^2$$

$$\frac{dE}{dk} = 2Ak$$

$$\frac{d^2 E}{dk^2} = 2A = 2 \times 10^{-31}$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

$$m^* = \hbar^2 \times \frac{1}{\left(\frac{d^2 E}{dk^2}\right)}$$

$$m^* = (1.05 \times 10^{-34})^2 \times \frac{1}{2 \times 10^{-31}}$$

$$\therefore m^* = 5.5 \times 10^{-38} \text{ kg.}$$

$$p = \frac{h}{\lambda}$$

$$= \frac{h \times 2\pi}{2\pi \times \lambda}$$

$$= \hbar \cdot k$$

$$p = (1.05 \times 10^{-34}) \times 10^{10}$$

$$p = 1.05 \times 10^{-24} \text{ kgms}^{-1}$$

Also,

$$p = mv$$

$$v = \frac{1.05 \times 10^{-24}}{5.5 \times 10^{-38}} = 1.9 \times 10^{13} \text{ m/s.}$$

$$E_h = \frac{1}{2} m^* v^2$$

$$= \frac{1}{2} \times 5.5 \times 10^{-38} \times (1.9 \times 10^{13})^2$$

$$= 9.9275 \text{ J}$$

Qs) The resistivity of an intrinsic semiconductor is $4.5 \Omega m$ at $20^\circ C$ and $2.0 \Omega m$ at $32^\circ C$. What is energy gap?

$$\sigma = n_i e (\mu_e + \mu_h)$$

$$= n_i e \mu$$

$$= \mu 2e \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_g}{2k_B T}}$$

$$\sigma_1 = C T_1^{3/2} e^{-\frac{E_g}{2k_B T_1}}$$

$$\sigma_2 = C T_2^{3/2} e^{-\frac{E_g}{2k_B T_2}}$$

$$\frac{\sigma_1}{\sigma_2} = \frac{T_1^{3/2} e^{-\frac{E_g}{2k_B T_1}}}{T_2^{3/2} e^{-\frac{E_g}{2k_B T_2}}}$$

Let, $T_1 = 20^\circ C$, $T_2 = 32^\circ C$, $\rho_1 = 4.5 \Omega m$, $\rho_2 = 2.0 \Omega m$
 $= 293 K$ $= 305 K$

or,

$$\frac{2}{4.5} = \frac{(293)^{3/2} e^{-\frac{E_g}{2k_B \times 293}}}{(305)^{3/2} e^{-\frac{E_g}{2k_B \times 305}}}$$

Taking ln on both sides

$$\text{or, } \ln\left(\frac{2}{4.5}\right) = \ln \left[(293)^{3/2} \times e^{-\frac{E_g}{2k_B \times 293}} \right] - \ln \left[(305)^{3/2} \times e^{-\frac{E_g}{2k_B \times 305}} \right]$$

$$\text{or, } \ln\left(\frac{2}{4.5}\right) = \ln(293)^{3/2} + \ln \left[e^{-\frac{E_g}{2k_B \times 293}} \right] - \ln(305)^{3/2}$$

$$-\ln [e^{-E_g/2k_B \times 305}]$$

$$\text{or, } -0.81 = 8.52 - \frac{E_g}{2k_B \times 293} - 8.58 + \frac{E_g}{2k_B \times 305}$$

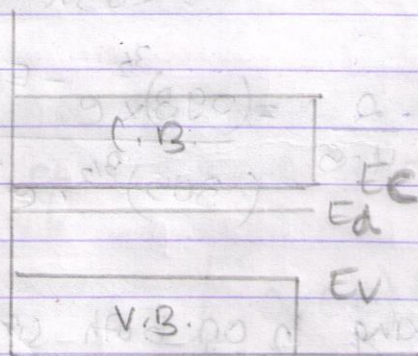
$$\text{or, } 0.75 = \frac{(305 - 293)E_g}{2 \times k_B \times 293 \times 305}$$

$$\text{or, } \frac{0.75 \times 2 \times 1.38 \times 10^{-23} \times 293 \times 305}{12} = E_g$$

$$\therefore E_g = 1.54 \times 10^{-19} \text{ J}$$

$$E_g = 0.9625 \text{ eV}$$

* concentration of electrons and fermi level in n type semiconductor



A n-type semiconductor is supposed to consist of a donor level of pentavalent impurity/element just below the bottom of conduction band. At 0K, all donor elements/donor atoms are unionized, but when the temperature is slightly increased, some of

the donor atoms get ionized and contribute electrons to the conduction band. At the same time, some electrons from valence band jump to conduction band leaving behind holes in v.B. But no. of holes are quite small. Thus, Fermi level must lie somewhere near middle of donor level and bottom of conduction band.

Let, there be N_d donors per unit volume occupying donor level E_d . Let E_F lies below the conduction band, then the electrons concentration in the C.B. is given by

$$n = N_c e^{(E_F - E_c)/k_B T} \quad \text{--- (1)}$$

Again,

Total no. of concⁿ in conduction band is given by

$$n = N_d^+ + p.$$

p = concⁿ of holes in v.B. generated thermally.

N_d^+ is concⁿ of ionised donors.

Here, p is very small. so, neglected. and we get,

$$n = N_d^+ = N_d - N_d^0.$$

N_d^0 = concⁿ of unionised donors.

$$N_d^0 = N_d \frac{1}{1 + e^{(E_d - E_F)/k_B T}}.$$

$$N_d^+ = N_d \left(1 - \frac{1}{1 + e^{(E_d - E_F)/k_B T}} \right)$$

$$= N_d \left(\frac{e^{(E_d - E_F)/k_B T}}{1 + e^{(E_d - E_F)/k_B T}} \right)$$

At room temp.

$$(E_F - E_d) \gg k_B T$$

$$(E_d - E_F) \ll k_B T$$

$$N_d^+ = N_d e^{(E_d - E_F)/k_B T}$$

Again $n = n_d^+ = N_d e^{(E_d - E_F)/k_B T}$ — (2)

From eqn (1) and (2), we have

$$N_c e^{(E_F - E_c)/k_B T} = N_d e^{(E_d - E_F)/k_B T}$$

Taking natural log on both sides, we get

$$\ln N_c + \frac{E_F - E_c}{k_B T} = \ln N_d + \frac{(E_d - E_F)}{k_B T}$$

$$\text{or, } \frac{E_F - E_c - E_d + E_F}{k_B T} = \ln \left(\frac{N_d}{N_c} \right)$$

$$\therefore \boxed{E_F = \frac{E_c + E_d}{2} + \frac{k_B T}{2} \ln \left(\frac{N_d}{N_c} \right)} \text{ — (3)}$$

This gives the position of Fermi level at

moderate temp. This shows that Fermi level lies near the middle of donor level and bottom of Conduction band. For increasing temp, Fermi level moves downward and crosses donor level.

For sufficiently large temperature, it drops to $\frac{E_g}{2}$ i.e. coincides with the intrinsic level.

In such case, extrinsic behaves like intrinsic semiconductor.

Again, from eqⁿ (1) and (3).

$$n = N_c e^{(E_F - E_C)/k_B T}$$

and from eqⁿ (3)

$$E_F = \frac{E_C + E_D}{2} + \frac{k_B T}{2} \ln\left(\frac{N_D}{N_C}\right)$$

Substituting this value of E_F in above eqⁿ, we get

$$n = N_c e^{\left[\frac{E_C + E_D}{2} + \frac{k_B T}{2} \ln\left(\frac{N_D}{N_C}\right) - E_C \right] / k_B T}$$

$$n = N_c e^{\left[\frac{E_C + E_D - E_C}{2 k_B T} + \frac{k_B T}{2} \ln\left(\frac{N_D}{N_C}\right) \times \frac{1}{k_B T} \right]}$$

$$n = N_c e^{\left[\frac{E_D - E_C}{2 k_B T} + \ln\left(\frac{N_D}{N_C}\right)^{1/2} \right]}$$

$$n = N_c e^{\left[\frac{E_D - E_C}{2 k_B T} \right]} \left(\frac{N_D}{N_C} \right)^{1/2}$$

$$n = N_c \left(\frac{N_D}{N_C} \right)^{1/2} e^{\frac{(E_D - E_C)}{2 k_B T}}$$

$$n = (N_c N_D)^{1/2} e^{-\Delta E / 2 k_B T}$$

where $\Delta E = E_c - E_d$ is the ionisation energy of donor level.

This shows that carrier concⁿ at moderate temperature varies as $\sqrt{N_d}$.

The electrical conductivity of N-type semiconductor is given by

$$\sigma = ne\mu_e$$

$$= N_d^+ e \mu_e$$

This eqⁿ is based on the assumption that conduction of electricity is due to electrons only.

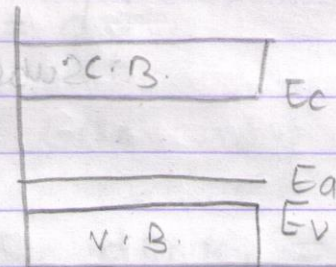
★ Carrier concentration, Fermi level in P-type semiconductor

Let us consider ' N_a ' be no. of acceptor impurities and

N_a^- is no. of ionised impurities

$n = \text{conc}^n$ of electrons in C.B.

$p = \text{conc}^n$ of holes in V.B.



We have

$$p = N_a^- + n$$

$$\therefore p = N_a^- \quad \text{①} \quad \text{[because } n \text{ is very less compared to } N_a^-]$$

The concⁿ of ionised acceptor is given by

$$N_a^- = \frac{N_a}{1 + e^{(E_a - E_F)/k_B T}} \quad \text{--- (2)}$$

At room temp

$$E_a - E_F \gg k_B T$$

$$E_F - E_a \ll k_B T$$

$$N_a^- = \frac{N_a}{1 + e^{-(E_F - E_a)/k_B T}}$$

neglecting 1.

$$N_a^- = N_a e^{(E_F - E_a)/k_B T} \quad \text{--- (3)}$$

Again,

$$p = N_v e^{(E_v - E_F)/k_B T} \quad \text{--- (4)}$$

From eqⁿ (1), (3) and (4)

$$N_a e^{(E_F - E_a)/k_B T} = N_v e^{(E_v - E_F)/k_B T}$$

Taking natural log and solving, we get

$$E_F = \frac{E_a + E_v}{2} - \frac{k_B T}{2} \ln \left(\frac{N_a}{N_v} \right)$$

This fermi level lies in the middle of acceptor level and top of the valence band. It moves upward with increase in temperature and finally coincides with intrinsic fermi level.

★ P-n junction.

→ The junction between p-type region and n-type region in the same semiconductor crystal is known as p-n junction.

~~P-n ju~~

In Si when penta valent impurity ^(P) like Phosphorus is added, P will be ionized by the thermal energy into the free form of $p^+ + e^-$.

One electron released from P atom will be quite free to move in crystal or it acts as charge carrier. This region is called N-region because electron is the charge carrier.

Similarly, when Boron is added in Si , B captures one electron from Si and Si atom is ionized by thermal energy. and thus B becomes B^- .

Si^+ ^{here} becomes lack of one electron
i.e. Si^+ , Si^+ can be written as
 $\text{Si}^+ = \text{Si} + p$ (one hole)

Here, hole will wander in the crystal and it behaves as charge carrier and this region is called p-region.

The picture of crystal doped with p-type

impurity and n-type impurity side-by-side with a sharp border line between two types of doping is shown in figure.

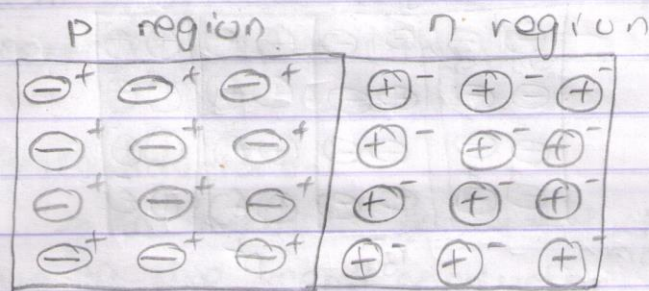


Fig (1) P-n junction before any reaction at zero bias.

In N-region, $\oplus$ represents positively charged Phosphorus, $-$ represents electrons i.e. charge carrier.

In P-region, $\ominus$ represents negatively charged Boron and $+$ represents holes i.e. charge carrier.

Fig (1) represents the stage of the prepⁿ of the crystal with doping when diffusion and recombination has not taken place between differently doped materials.

Now, the electron from N-type diffuse through the border line towards the p-type region and combine with hole annihilating each other. Similarly, holes from the P-region will diffuse through the border towards N-region and will combine with the electron and both vanish. The resulting pic-

ture will be that on the left of junction, there will be negatively charged B^- ion and on the right, there will be positively charged P^+ ion.

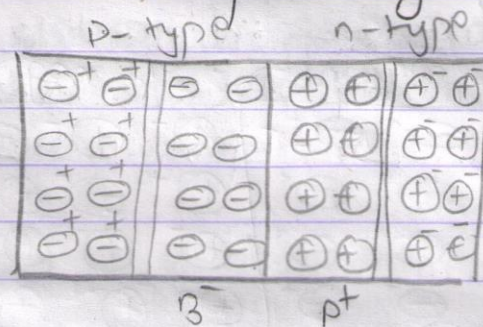


Fig: PN junction with zero bias in thermal eq^m.

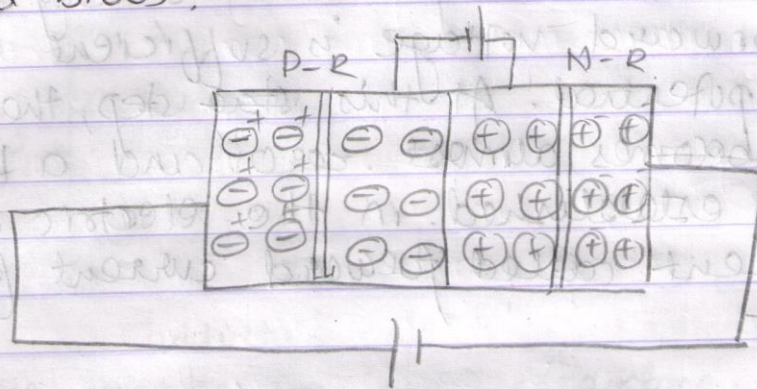
Accumulation of the '-ve' charge on the border of P-region after certain limit will restrict further diffusion of the electrons towards the P-region.

The limited region in which only ions are present [negative ions on left side and positive ions on the right side of the junction] is called the depletion layer which is order of $10^2 - 10^6$ Å with width.

Due to accumulation of negative ions in one side and positive ions in another side, depletion layer is equivalent to battery of voltage 0.7 V for silicon and 0.3 V for Ge.

★ Effect of External Voltage on the width of Depletion layer.

1) Forward bias

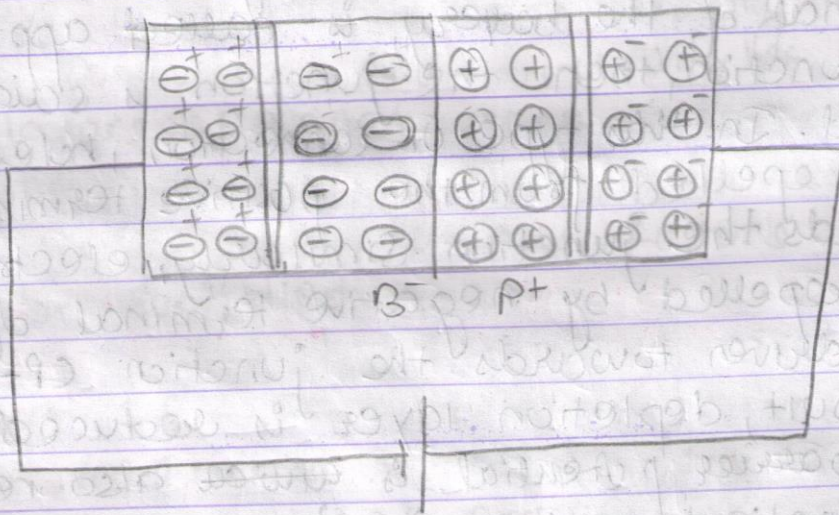


When an external field with P-region connected to positive terminal and N region connected to negative terminal of the battery, is ~~called~~ applied across the junction, then the junction is said to be forward biased. In this type of connection, holes in P-region are repelled from the positive terminal and driven towards the junction. Similarly, electrons in N-region are repelled by negative terminal of the battery and driven towards the junction (P-region). As a result, depletion layer is reduced in width and barrier potential is ~~also~~ also reduced. If the applied voltage is increased, barrier potential gets progressively smaller and smaller until it effectively disappears and charge carriers can easily flow across the junction.

Electrons from N-region are attracted across by positive terminal on the P-side and holes are attracted by negative terminal on the N side. Thus, ~~a~~ majority carriers current flows.

Since, barrier potential is very small, a small forward voltage is sufficient to eliminate barrier potential. At this ~~step~~ step, the junction resistance becomes almost zero. and a low resistance path is established. in the electric circuit. and the current called forward current flows in the circuit.

2) Reverse bias



If an external bias voltage is applied with positive terminal connected to N-region and negative terminal connected to P-region of p-n junction, the junction is said to be reverse biased.

In this case, electrons from N-region are attracted to the positive terminal of battery and holes are attracted to the negative terminal of the source, increasing the dep-

pletion layer and potential barriers. With this, there is no majority carrier current flow ~~across~~ across the junction. Thus, P-N junction is in "non-conductive ~~stage~~ state".

★ Energy bands of semiconductor with P-N junction.

When two types of semiconductor are kept in intimate contact, the separate ~~fermi~~ fermi levels of the two types of semiconductors merge into a single level ~~at~~ adjustment and combining of fermi level into a single level ensure $\leq$ minimum energy condition for the semiconductor.

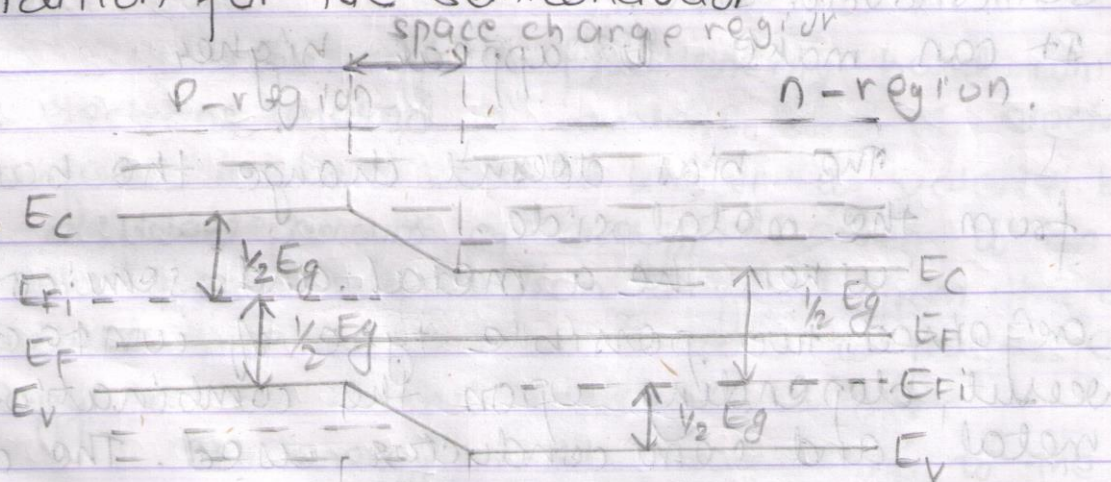


Fig. Energy band diagram of P-N junction in thermal equilibrium.

Metal semiconductor junction

When metal and semiconductor are in intimate contact, then the junction is called metal semiconductor junction. In junction, there exist a potential barrier between them that prevents most charged carriers ~~from~~ passing from one to another. Only a small number of carriers having enough energy get over the barrier and cross to the other material.

When biased is applied to the junction, it can have one of the two effects:

- i) It can make the barrier appear lower from the semiconductor side.
- ii) It can make to appear higher.

The bias doesn't change the barrier from the metal side.

When a metal and semiconductor are joined, two possible type of contact can result, depending upon the combination of metal and semiconductor used. The contact may be rectifying which allows current to pass in one direction. Alternatively, it could be ohmic in which, ~~more~~ current can pass in either direction.

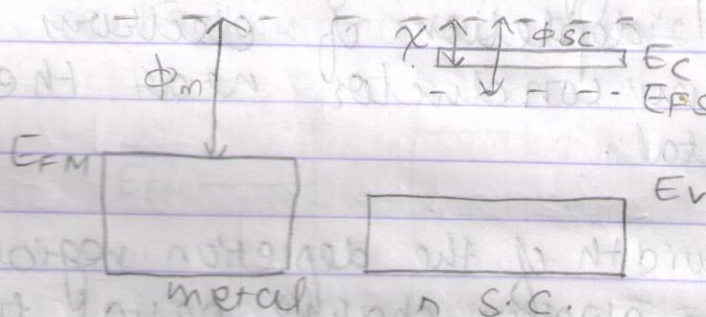
① Schottky contact diode.

A Schottky contact is formed when a ~~rectifying~~ rectifying contact is formed between

the metal and semiconductor.

Let N-type semiconductor and metal are contacted and their energy band diagram are as shown below.

Before contact -



The work function of the semiconductor is required to extract an electron, located at its Fermi level E_{FSC} .

Here, Φ_m = work function of metal.

Φ_{sc} = work function of semiconductor.

We know that, in a semiconductor, some electrons have higher energy than E_{FSC} . These can be found in conduction band and their energy is nearly equal to E_C . The energy needed to extract an electron from the conduction band into a vacuum is called the electron affinity and denoted by χ .

Here, $E_{FM} < E_{FSC}$ and when metal

is contacted with the semiconductor, the Fermi levels align and thermodynamic ~~also~~ equilibrium is established through the transfer of electrons from semiconductor conduction band into metal as $E_c > E_{Fm}$.

These electrons leave behind positively charged atom impurity in the semiconductor. Therefore, a zone of depletion of electrons is formed in the semiconductor near the interface of the metal.

The width of the depletion region is denoted by w_0 . An electron charge equal to the depletion charge appears in the metal. Such a charge distribution is called charge sheet.

Because of the alignment of Fermi level and presence of a depletion region, the band curvature in the semiconductor is equal to

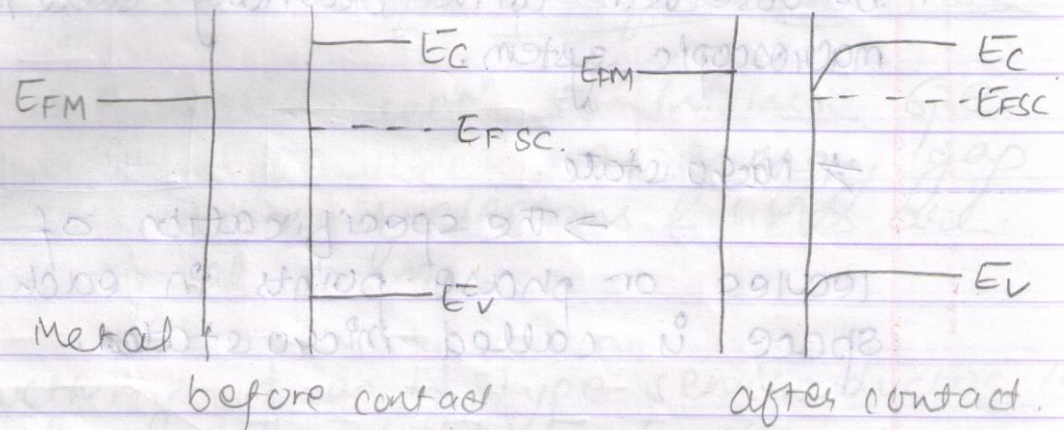
$$V_i = \Phi_m - \Phi_{sc}$$

This ' V_i ' prevents further electrons from migrating into the metal.

② Ohmic contact

It is a non-rectifying contact. It obeys Ohm's law $V = IR$, and the resistance of

the contact should be as low as possible. Consider a ~~metal~~ contact betⁿ metal and semiconductor in which $E_{FM} > E_{FSC}$ such that ^{energy band of the} N type semiconductors are bent downward near the contact. The magnitude of the band bending and its extension into the semiconductor is very small. As a result, there's ~~no~~ virtually no potential barrier and electrons can flow freely through the contact. Such a contact is called ohmic contact.



Statistical Mechanics

★ Microscopic system

→ A system of atomic dimension or of smaller size is called a microscopic system.
Eg. Molecule.

★ Macroscopic system

→ A system which is large enough to be observed with ordinary scale/sense is called macroscopic system.

★ Micro state

→ The specification of number of molecules or phase points in each cell of phase space is called micro states.

★ Micro state

The specification of the states of the constituent particles of the given system is called micro state.

Qs) Four distinguishable coins are tossed for a large number of times. Write down the different microstates which may be observed and the macrostates into which they would fall. Write down the probability of the most probable macrostate.

→ $2^4 = 16$
a, b, c, d

Microstate		Macro state	
Coins with head	Coins with tail	no. of heads n_1	no. of tails n_2
abcd	d	4	0
abc	c	3	1
abd	c	3	1
acd	b	3	1
bcd	a	3	1
ab	cd	2	2
bc	ad	2	2
ac	bd	2	2
cd	ab	2	2
bd	ac	2	2
ad	bc	2	2
d	abc	1	3
c	abd	1	3
b	acd	1	3
a	bcd	1	3
0	abcd	0	4

heads tail

$n_1 = 2$ and $n_2 = 2$

Microstates 6
 Macrostates 16 = 2^4

Phase space

Specification of the microstate of a system containing the n particles requires $3N$ position co-

coordinates

$$q_1, q_2, \dots, q_{3N}$$

and $3N$ momentum co-ordinates.

$$p_1, p_2, \dots, p_{3N}$$

The set of coordinates $(q_i, p_i; i = 1, 2, \dots, 3N)$ may be regarded as a point of $6N$ dimension, which is called phase space or Γ -space.

As the time passes, the set of co-ordinates (q_i, p_i) undergoes a continuous change. The representative points in the phase space, then curves a trajectory which is called a phase space trajectory.

6 dimensional space where specification of a molecule is possible is called a phase space or μ space. The elementary volume of that phase space is called cell.

If we consider a molecule, then to specify it, we require three coordinates dx, dy and dz and three momenta say dp_x, dp_y and dp_z . The volume element in the phase space is given by

$$d\Gamma = dx dy dz dp_x dp_y dp_z$$

But from Heisenberg's uncertainty principle,

$$\Delta x \Delta p_x \geq \frac{h}{2\pi}$$

Similarly,

$$\Delta t \Delta E \geq \frac{h}{2\pi}$$

★ Phase space of an one-dimensional harmonic oscillator.

Qs) Consider a case of simple harmonic oscillator is one-dimensional microcanonical ensemble. Show that the area in phase space is equivalent to one eigen state i.e. $2\pi\hbar$.

→ Let us consider harmonic oscillator of mass 'm' and spring constant 'k'. and total energy is

$$E = K.E + P.E$$

$$E = \frac{P^2}{2m} + \frac{1}{2} k q^2$$

$$\text{or, } \frac{p^2}{2mE} + \frac{q^2}{2E/k} = 1 \quad \text{--- (1)}$$

which is equation of ellipse in p q space. Comparing eqn (1) with standard equation of ellipse

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad , \text{ we get}$$

$$\text{Semi major axis} = \sqrt{2mE}$$

$$b = \sqrt{\frac{2E}{k}}$$

The area of oscillator in phase space is given by πab .

$$A = \pi \sqrt{2mE} \cdot \sqrt{\frac{2E}{k}}$$

$$A = 2\pi E \sqrt{\frac{m}{k}} \quad \text{--- (2)}$$

Frequency of the oscillator is given by

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$T = 2\pi \sqrt{\frac{m}{k}}$$

$$\sqrt{\frac{m}{k}} = \frac{1}{2\pi f} \quad \text{--- (3)}$$

From (2) and (3)

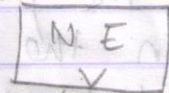
$$\textcircled{1} \quad A = 2\pi E \cdot \frac{1}{2\pi f}$$

$$A = \frac{E}{f} = hf = \frac{2\pi h E}{2\pi}$$

$$= 2\pi h$$

★ Ensemble.

NE ✓	NE ✓	NE ✓	NE ✓
NE ✓	NE ✓	NE ✓	NE ✓
NE ✓	NE ✓	NE ✓	NE ✓
NE ✓	NE ✓	NE ✓	NE ✓



System of interest.

A collection of a very large number of system, each constructed to be a replica of thermodynamic system of interest is called an ensemble.

OR

The ~~random~~ collection of gas molecules form the assembly, Random collection of identical and independent assemblies is called ensemble.

All the members in ensemble which are identical in features like N , E , V are called elements of that ensemble.

There are three types of ensemble.

- Density ★
- ① Microcanonical ensemble.
 - ② Canonical ensemble.
 - ③ Grand canonical ensemble.

★ Density function: The overall movement of the

representative point in the phase space can be illustrated in terms of density function $S(q, p, t)$. This function is defined as $S(q, p, t) d^{3N}q d^{3N}p =$ the probability of the state point (q, p) lies in the volume element $d^{3N}q d^{3N}p$ at any instant of time.

Constraints.

→ The condition imposed in the selection of system ensembles, etc., are called constraints.

OR

→ The restrictions employed in the selection of parameters is called constraints.

For example,

$$N = \sum n_i = \text{constant}.$$

$$E = \sum n_i \epsilon_i = \text{constant}.$$

Accessible states are the states consistent with the given constraints given to the system.

Thermodynamic probability.

It is defined as the number of microstates corresponding to that macrostate. It is denoted by Ω .

Consider two cells in phase space represented by i and j and four phase points a, b, c, d . Let N_i and N_j be the phase points in i and j cells respectively. Then, the possible

macrostates are :

N_i	4	3	2	1	0
N_j	0	1	2	3	4

Here, total number of macrostates are 5.

Let us consider the microstates corresponding to the macrostates $N_i = 3, N_j = 1$.

cell i	abc	abd	bcd	cda
cell j	d	c	a	b

microstate = 4

Hence, the probability of macrostate in $N_i = 3, N_j = 1$ is $\frac{1}{4}$ as no. of microstates is 4.

In general case of N phase points, total no. of permutations is $N!$. If But if n_1 be no. of phase points in cell 1, n_2 in the cell 2 and so on, then there are $n_1!$ in cell 1, $n_2!$ in cell 2 and so on, then thermodynamic prob. is given by.

$$\Omega = \frac{N!}{n_1! n_2! \dots}$$

$$S = k_B \ln \Omega = k_B \ln \left(\frac{N!}{n_1! n_2! \dots} \right)$$

$$P = \frac{S}{k_B} = \ln \Omega$$

$$S = k_B P = k_B \ln \Omega$$

consider a system of 3 cells such that $n_1 = 6$,
 $n_2 = 4$ and $n_3 = 3$ & $E_1 = 0$, $E_2 = 2$ Joules
 per particle

$E_3 = 4$ Joules per particle

If $\delta n_3 = -2$, find δn_1 , δn_2 assuming
 N & E to be constant. Also find the initial
 & final probabilities

so n :

$n_1 = 6$	$n_2 = 4$	$n_3 = 3$
-----------	-----------	-----------

$$E_1 = 0 \quad E_2 = 2 \quad E_3 = 4.$$

$$N = n_1 + n_2 + n_3 = 6 + 4 + 3 = 13.$$

Again,

$$\delta n_3 = -2.$$

$$\delta n_1 + \delta n_2 + \delta n_3 = 0$$

$$\text{or, } \delta n_1 + \delta n_2 - 2 = 0$$

$$\delta n_1 + \delta n_2 = 2.$$

$$E = E_1 n_1 + E_2 n_2 + E_3 n_3$$

$$= 0 + 2 \times 4 + 4 \times 3$$

$$= 20 \text{ J.}$$

$$\text{Also, } 0 + 2 \delta n_2 + 4 \delta n_3 = 0.$$

$$\delta n_2 = -2 \delta n_3$$

$$\delta n_2 = -2 \times -2 = 4.$$

$$\therefore \delta n_1 = 2 - 4 = -2.$$

$$N = n_1 + \delta n_1 + n_2 + \delta n_2 + n_3 + \delta n_3$$

$$= 6 + 2 + 4 + 4 + 3 + 2$$

$$= 4 + 8 + 1$$

$$= 13$$

$$\therefore \Omega = N!$$

$$n_1! n_2! n_3!$$

$$= 13!$$

$$\Omega = 9$$

$$6! 4! 3!$$

$$\Omega$$

$$=$$

$$\Omega' = \frac{N!}{n_1! n_2! n_3!}$$

$$n_1! n_2! n_3!$$

$$\Omega' = \frac{13!}{4! 8! 1!}$$

$$= 6435$$

$$= 6435$$

Types of ensemble.

① Microcanonical ensemble.

(N, V, E ensemble)

→ It is a collection of equivalent closed and isolated systems of a very large no. of particles. A system is closed and isolated if it translates neither particle nor energy with its surrounding. Hence, each system in a microcanonical ensemble has N -particles in volume V with energy E between E and $E + \Delta E$.

In terms of density function, microcanonical ensemble is defined by the collection of systems such that density function $\rho(p, q) = \text{constant}$ for certain energy range and $\rho(p, q) = 0$; otherwise

The probability of microstates in a given macro state of microcanonical ensemble is

$$P = \frac{1}{\omega}$$

where ω is no. of microstates within an energy range.

② Canonical ensemble (NVT ensemble)

→ A canonical ensemble describes those systems which are not isolated but are in contact with the heat bath under consideration and, then the system of ~~considerate~~ interest is ~~present~~ treated as the sub-system of the close system.

The system can exchange energy with a heat bath so that various possible states of the system can differ in total energy.

Probability of microstates in canonical ensemble is given by.

$$P = \frac{e^{-(F-E)}}{k_B T}$$

where, $F = \text{Helmholtz free energy} = U - TS$

where S is entropy

(3) Grand canonical ensemble (μ, V, T ensemble)

→ An open system can exchange both heat and matter with the surrounding and therefore, both the energy and particle number will fluctuate. Such an ensemble having μ, V and T fixed and E, N fluctuating is called a grand canonical ensemble.
where, μ = Chemical potential.

Probability of microstates in this ensemble is

$$P = e^{-\frac{(\Omega + \mu N - E)}{k_B T}}$$

where, Ω is Grand potential constant.

μ is chemical potential